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Electronegativity of Organic Radicals in Organometallic Compounds

By E. B. TOWNE*

ONE of the most direct and comprehensive methods for determining the relative reactivity or electronegativity of radicals is that based on the cleavage of unsymmetrical organometallic compounds by halogen acids, in which the more negative of two radicals is preferentially cleaved. The cleavage results are, in general, the same whether organomercury, -lead, or -tin compounds are used. The following reactions illustrate the method:

(I) $C_2H_5HgC_6H_5 + HCl \longrightarrow C_2H_5HgCl + C_6H_6$

(II) $(C_6H_5)_3PbCH_2C_6H_5 + HCl \longrightarrow (C_6H_5)_2(C_6H_5CH_2)PbCl + C_6H_6$

(III) $(C_2H_5)_3SnCH_2C_6H_5 + HCl \longrightarrow (C_2H_5)_2(C_6H_5CH_2)SnCl + C_2H_6$

These results give a simple series of radicals arranged in the order of decreasing negativity as follows:

$$C_6H_5- > C_2H_5- > C_6H_5CH_2-$$

Similar cleavage reactions involving many different radicals have made it possible to expand this into the more general series:

aromatic > aliphatic > substituted aliphatic—

which agrees, in general, with reactivity series determined by other methods.

Since the splitting of unsymmetrical organometallic compounds with halogen acids or halogens is the most typical reaction of these compounds, it is not surprising that many early workers began arranging radicals in the order of their ease of cleavage. Among those working with organolead compounds were Möeller, Peiffer, Grüttner, and Krause; while Ladenburg, Kipping, Kraus, and Bullard worked with organotin compounds. Many of these workers used halogens rather than halogen acids but the series of radicals obtained was the same, with the exception of the benzyl radical. With halogen acids, the methyl group is split off in preference to the benzyl, while with halogens the reverse is true. This anomalous behavior of the benzyl radical with halogens has occasioned considerable controversy; one explanation assumes that oxidation or substitution precedes the cleavage with halogens.

Kharasch and coworkers (*1*) have done most of the work on the cleavage of unsymmetrical organomercury compounds (Reaction I) and have compiled an imposing electronegativity series of radicals, which is given in part in Table I (Page 2). The radicals are arranged in the order of decreasing negativity.

Kharasch's concept of electronegativ-

*Kodak Research Laboratories, Rochester 4, N. Y.

TABLE I
KHARASCH'S ELECTRONEGATIVITY SERIES OF RADICALS

$-CN > p-CH_3O\cdot C_6H_4- > o-CH_3O\cdot C_6H_4- > \alpha-C_{10}H_7- > o-CH_3\cdot C_6H_4- >$
$p-CH_3\cdot C_6H_4- > m-CH_3\cdot C_6H_4- > C_6H_5- > p-Cl\cdot C_6H_4- > o-Cl\cdot C_6H_4- >$
$m-Cl\cdot C_6H_4- > CH_3- > C_2H_5- > C_3H_7- > (CH_3)_2CH- > n-C_4H_9- > iso-C_4H_9- >$
$n-C_7H_{15}- > C_6H_5\cdot CH_2- > C_6H_5\cdot CH_2CH_2- > (CH_3)_3C- > (C_6H_5)_3C-$

ity is based on the view that in the compound R′HgR, the more negative radical R′ holds its bonding electron-pair more closely or firmly and therefore combines more readily with the H^+ of the HCl and splits off as R′H, while the Cl^- then combines with the RHg− residue to give RHgCl.

An examination of the electronegativity series in Table I shows that the aromatic radicals are more negative than aliphatic radicals, and that the latter, in turn, are more negative than phenyl-substituted aliphatic radicals. Among the aromatic radicals, those less negative than phenyl can be formed by direct substitution, while those more negative than phenyl cannot be so formed. Among the aliphatic radicals, lengthening or branching the carbon chain decreases the negativity; thus, secondary and tertiary groups are less negative than the corresponding normal radicals. The introduction of a phenyl group into an aliphatic radical greatly decreases the negativity; e.g., benzyl.

Kharasch (*2*) has pointed out in a number of papers numerous ways in which the electronegativity series can be used in predicting chemical reactions. For example, the series has been used to predict the stability of organometallic compounds, the mode of addition of HX to substituted olefins, and the dissociation of hexaaryl ethanes, with good results.

Whitmore (*3*) has split some unsymmetrical organomercury compounds and has determined the position of a number of branched chain aliphatic radicals in this series with results in conformity with Kharasch's findings.

In considering the general series (aromatic > aliphatic > substituted aliphatic), the question arises as to what position heterocyclic and unsaturated aliphatic radicals occupy.

Recent work with organolead compounds (*4*) (Reaction II) has placed some heterocyclic radicals in the electronegativity series. These cleavage experiments showed that the 2-furyl radical was split off in preference to the 2-thienyl, p-anisyl, and phenyl radicals, giving the series:

$2-C_4H_3O- > 2-C_4H_3S- > p-CH_3O\cdot C_6H_4- > C_6H_5-$

Since the p-anisyl radical stands at the top of Kharasch's series, these results show the 2-furyl radical to be the most negative group so far studied.

Other cleavage experiments on unsaturated organolead compounds (*5*, *6*) showed that the allyl, β-styryl, and phenylacetenyl radicals were split off in preference to phenyl, demonstrating that these olefinic radicals stand well toward the top of the electronegativity series. On the other hand, the phenyl and ethyl radicals were cleaved in preference to the 3-butenyl ($CH_2=CHCH_2CH_2-$) and 4-pentenyl ($CH_2=CHCH_2CH_2CH_2-$) radicals, showing the latter radicals to stand well toward the bottom of the electronegativity series. These results indicate that olefinic radicals fall into two classes, one more negative than phenyl, the other less negative than phenyl, depending on the position of the double bond with respect to the carbon-metal linkage. These cleavage results with unsaturated aliphatic radicals give the following series in the order of decreasing negativity:

$(CH_2=CHCH_2-$, $C_6H_5\cdot CH=CH-$,
$C_6H_5\cdot C\equiv C-) > C_6H_5- > C_2H_5- >$
$(CH_2=CHCH_2CH_2-$, $CH_2=CHCH_2CH_2CH_2-)$

Kharasch has long held that the allyl radical is a relatively positive group like the benzyl. In order to explain the clear-cut cleavage of allyl in preference to phenyl above, he postulates that H^+ adds to the allyl double bond, giving $CH_3\overset{+}{C}HCH_2-M-R$ prior to the carbon-metal cleavage (*1d*). If this mechanism is confirmed, the cleavage method would not be valid for comparing the negativity of allyl with other radicals.

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A New Reagent for the Purification and Identification of Alcohols

By C. D. ROBESON*

THE compound p-Phenylazobenzoyl chloride (*1*), $C_6H_5N=NC_6H_4COCl$ forms readily crystallizing esters with alcohols and phenols and has thus proved an effective reagent for their purification. For example, pure beta tocopherol was isolated from wheat germ oil as the azobenzene carboxylate (Fig. 1) (*2*) when efforts to crystallize a variety of other derivatives had failed.

The azoyl esters are especially suited to purification by chromatography because their orange or reddish colors produce bands which are easily distinguished on the column. In this way colorless hydroxylic compounds can be visually tagged during purification by adsorption. The reagent is also suited to the purification of mixtures of hydroxylic materials since the individual esters can frequently be differentiated on the adsorption column.

Separations which have been accomplished by the azoyl reagent are numerous. For example, mixtures of ergosterol, cholesterol, and stigmasterol have been separated by the combination of esterification and chromatography (*3*). Several pairs of sugars including α-*d*-glucose and sucrose have been separated by

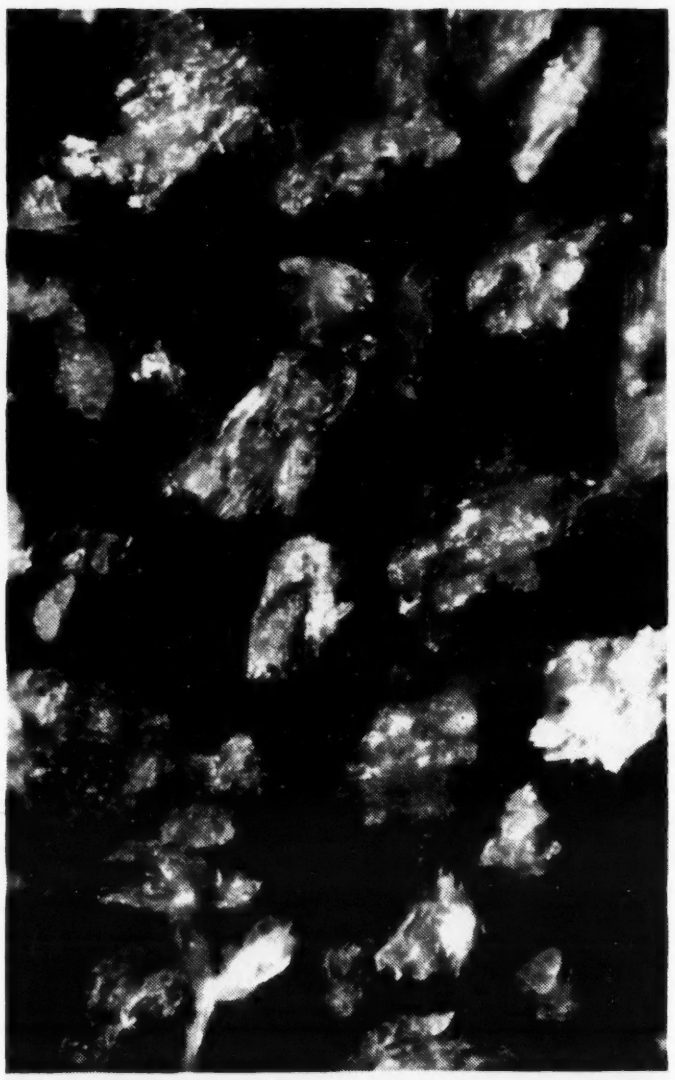

Fig. 1—*β-Tocopherol Azobenzene-4-carboxylate × 25*

*Distillation Products Inc., Rochester 13, N. Y.

chromatographic adsorption of the esters on magnesol and silicic acid (*4*). In one chromatogram a separation of four azoates, β-*l*-arabinose, β-*d*-glucose, α,α-trehalose, and β-cellobiose, was accomplished (*5*). The azoyl derivatives of glycine, alanine, leucine, and valine methyl esters also have been separated in this way, zinc carbonate being used as the adsorbent (*6*).

Thus, the ready adaptation to chromatographic purification, as well as the good crystallizing properties of the azoyl derivatives, promises to make p-phenylazobenzoyl chloride an increasingly useful reagent to the organic chemist.

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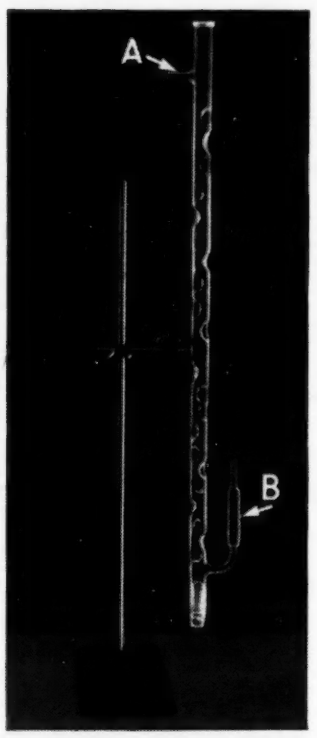
A Gas Absorber Column

CORROSIVE GASES are sometimes evolved from reactions in chemical laboratories when a hood is either unavailable or not practicable. A gas absorber column which has been used successfully in such instances is illustrated.

This apparatus consists of a glass tube, 1¼ inches in diameter and about 4 feet long, with indentations arranged spirally throughout most of its length. A water inlet, *A*, and a vent are located at the top, and the gas inlet, *B*, and a water outlet at the bottom. The outlet may be trapped as illustrated, or the trap can be made removable by means of a rubber stopper. A simpler type of trap is a beaker of water in which the lower end of the tube is immersed. An expansion tube is included in the gas inlet tube to prevent water from backing into the gas line.

The counter-current washing effect of water in a tube at least 3 feet long is very efficient. This effect can be increased by using two or more tubes in a series.

Absorbers of this type have been used successfully for the absorption of hydrogen chloride and sulfur dioxide from thionyl chloride reactions, hydrogen chloride from Friedel-Crafts reactions, chlorine from chlorinations, hydrogen bromide from brominations, and the nitrogen oxides from oxidations.



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P 5519	3,4-Dichlorotoluene (Pract.) BP 206-207° ..... $Cl_2C_6H_3CH_3$	1 kg.	3.30 E